Reducing Groundwater Conditions at Forest-Products Industry Sites: 2. Field Water-Quality Measurements

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Reducing-Environment Groundwater

- Lab indicators
  - High dissolved organic carbon
  - High color
  - High iron, manganese
  - No nitrate
  - Little to no sulfate
  - Poor cation-anion balance
- Field indicators
  - Colored sample
  - DO <1 to 0 mg/L
  - Negative redox

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Understand the Site Hydrogeology

- Utilize existing on-site and off-site data
- Make good observations during drilling
- Aquifer Tests

  "We dropped a slug into the well and measured its response."

No animals were injured during preparation of this image

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Always get an accurate water-level measurement

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Oxidation-Reduction Potential (ORP)

- Geochemical indicator
- Redox potential (Eh)
  - \+ Oxidizing
  - \- Reducing
- Measure in the field with a redox electrode (platinum or silver)
- Use a flow cell
- Or, measure DO, Fe(II), and sulfide

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Dissolved Oxygen (DO)

- O_2 solubility in water ~ 8 to 11 mg/L
- Groundwater DO generally below O_2 solubility
- DO Meter (electrometric method)
  - Meters use a membrane-type probe, carry spare membranes and filling solution
  - Calibrate meter using humid air in a bottle
  - Do not allow sample to come into contact with air--use a flow cell
  - Subject to interferences in reducing environments
- Field test kit (colorimetric method)
  - Ampoules
  - May have color interferences

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Field Iron Measurements

- Fe II--ferrous iron
- Fe III--ferric iron
- If total Fe > ~1mg/L, DO < 0.5 mg/L, Fe II will be major form
- CHEMetrics test kits
  - Ferrous Iron (<10 mg/L)
  - Ferrous and Total Iron (to 250 mg/L)
  - Filter the sample before doing the test
  - Takes 1-2 minutes per test
- HACH Spectrophotometer
  - 1,10-Phenanthroline method

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Field Iron Measurements

	Field					Lab	
Site ID	pH (units)	DO (mg/L)	Iron(II) (mg/L)	Iron (mg/L)	Iron(II) (%)	Iron, diss (mg/L)	Iron, total (mg/L)
LMW-03A	6.9	0.2	3.70	4.80	77%	4.35	4.39
LMW-04A	6.0	6.0	0.04	0.27	15%	<0.050	0.05
LMW-04B	8.3	0.3	0.04	0.06	67%	<0.050	<0.050
LMW-06B	7.3	--	2.30	9.00	26%	11.0	12.4
LMW-14D	6.8	0.5	2.40	2.69	89%	2.70	2.84
LMW-14S	6.7	0.4	3.20	5.16	62%	4.84	5.31
LMW-15S	7.2	0.3	0.08	0.10	80%	0.27	0.59
LMW-17D	7.5	--	3.70	6.50	57%	8.89	8.95
LMW-17S	7.2	--	4.30	8.70	49%	9.59	11.4
LMW-18D	7.4	0.3	0.06	0.07	86%	<0.050	<0.050
LMW-18S	6.6	0.5	10.28	12.64	81%	11.7	12.4

Field iron (II) and total iron analyses by HACH 1,10-phenanthroline spectrophotometric method

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Field Alkalinity

- Use HACH Digital Titrator with pH meter
- 0.16 or 1.6 N H_2SO_4
- 50 mL filtered sample
- Titrate to about pH 3.8; use small increments of acid around pH 10, 8.3, and 4.5
- Takes 10-30 minutes/sample
- Use USGS Alkalinity Web Calculator
  http://oregon.usgs.gov/alk/

Titration endpoints: Hydroxide (pH ~ 10.5); Carbonate (pH ~8.3); Bicarbonate (pH ~4.5)

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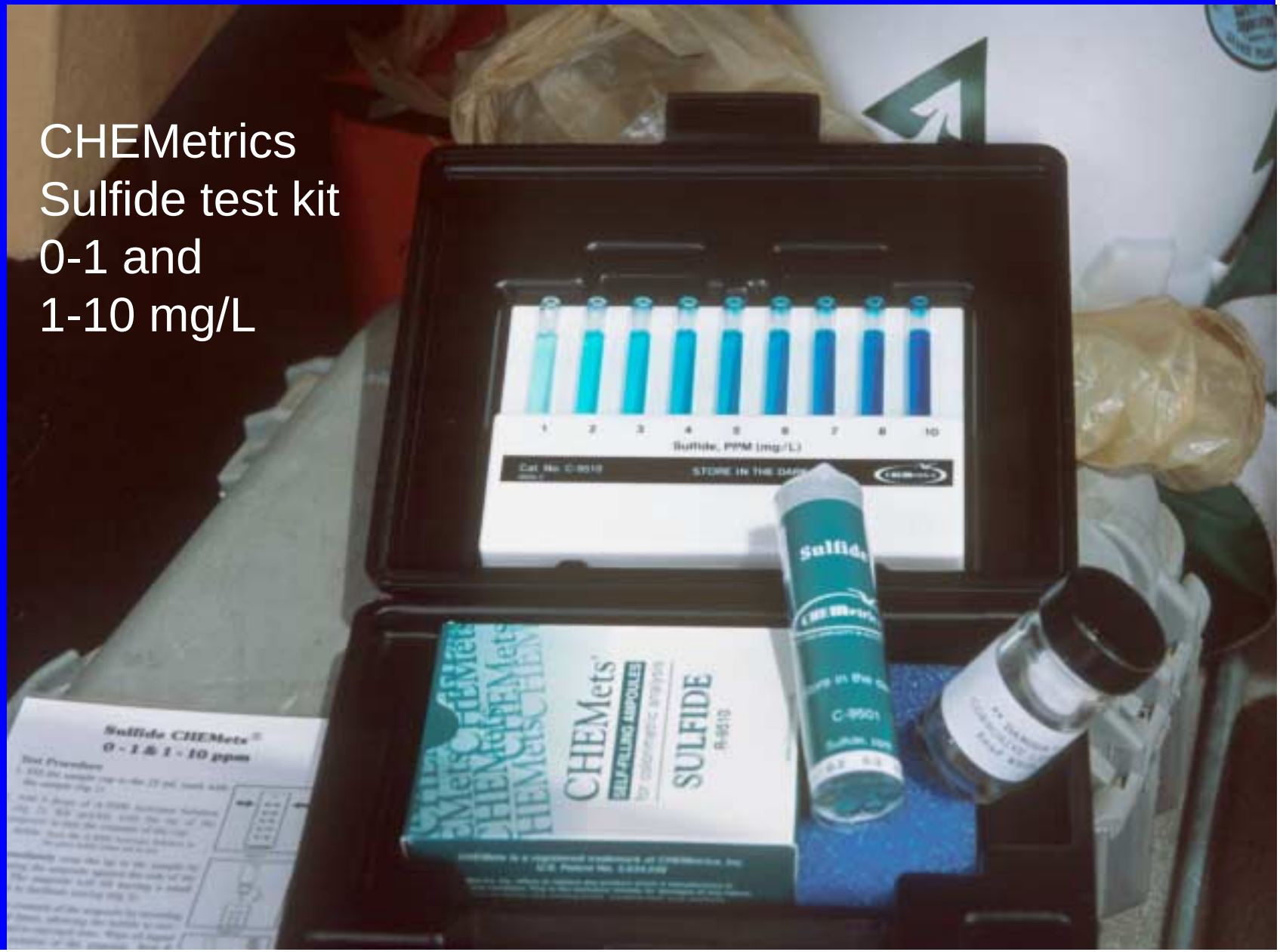
Sulfide



CHEMetrics
Sulfide test kit
0-1 and
1-10 mg/L

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Cation-Anion Balance Check

- Convert from mg/L to milliequivalents per liter

  meq/L = ionic mass divided by the valence
- Sum the cations ($\sum$ cations)
- Sum the anions ($\sum$ anions)
- Ionic balance (% difference) =

  $$100\ (\sum \text{cations} - \sum \text{anions}) / (\sum \text{cations} + \sum \text{anions})$$
- ±10% is ok; ±5% is better in aerobic environment
- May be off by 50% or more in reducing environment

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Common Data Check: Cation-Anion Balance

- Factors affecting cation-anion balance
  - Fe(II) about 1 - 200 mg/L
  - Possible iron carbonate, sulfate, or chloride precipitate after sample collection (recently saw iron oxide and iron phosphate precipitation 2 hrs after sample collection)
  - Lab vs. field alkalinity (no hold time)
  - Need sulfide concentration
- Balance can not be used as a reliable lab QA method in reducing conditions
- And then there are bad laboratory methods...

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Tannins and Lignins (SM 5550)

- Required by many permits
- Method responds to many substances
  - Ferrous iron, manganous ion, sulfide, canide, nitrate, sugars, humics
- No tannin-lignin standard
- Response depends on standard used
- The method even says “interpret such results with caution” if the types of tannins present in the water sample are unknown
- Don’t use this method. Ever.

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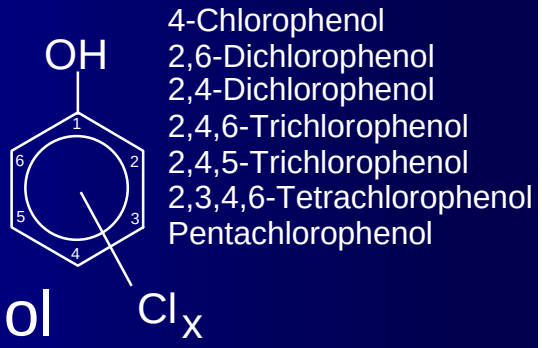
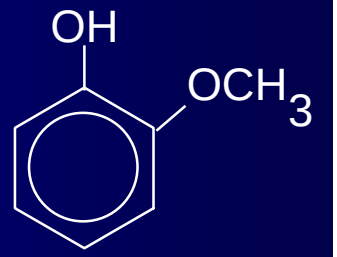
Phenols by 4-Amino-Antipyrene

- SW-846 9065/9066; SM 5530 (4-AAP)
- Phenolic compounds react with different efficiencies
- Substituted phenolics don't react like phenol
  - Pentachlorophenol is not measured
- 4-AAP test method creates phenolics
  - Acid distillation of sample at >100°C
  - Humic or wood extractives create compounds similar to phenolics (e.g. guaiacol)
- GC/MS fails to confirm these phenolic compounds (Neufeld and Paladino, 1985)



4-Chlorophenol
2,6-Dichlorophenol
2,4-Dichlorophenol
2,4,6-Trichlorophenol
2,4,5-Trichlorophenol
2,3,4,6-Tetrachlorophenol
Pentachlorophenol



Guaiacol

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